



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : <b>H01L 51/20</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 99/31741</b></p> <p>(43) International Publication Date: 24 June 1999 (24.06.99)</p>
<p>(21) International Application Number: PCT/IB97/01565</p> <p>(22) International Filing Date: 15 December 1997 (15.12.97)</p> <p>(71) Applicant: INTERNATIONAL BUSINESS MACHINES CORPORATION [US/US]; Old Orchard Road, Armonk, NY 10504 (US).</p> <p>(72) Inventors: KIEWRA, Edward, W.; 337 Cooper Drive, Verbank, NY 12585 (US). ROENTGEN, Peter, Berghaldenstrasse 44, CH-8800 Thalwil (CH). SEIDLER, Paul, F.; Obstgartenstrasse 12, CH-8136 Gattikon (CH).</p> <p>(74) Agent: HEUSCH, Christian; International Business Machines Corporation, Säumerstrasse 4, CH-8803 Rüschlikon (CH).</p>		<p>(81) Designated States: European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With international search report.</p>
<p>(54) Title: COMPOUND-METAL CONTACTS FOR ORGANIC DEVICES AND METHOD FOR MAKING THE SAME</p> <p>(57) Abstract</p> <p>Organic electroluminescent device comprising a substrate, an anode, a cathode, and an organic stack being sandwiched between the anode and cathode. The cathode of this organic electroluminescent device comprises a metallic compound, wherein the metallic compound is a carbide, nitride, or boride of an early transition metal, lanthanide or alkaline earth (group IIA of the periodic table of elements).</p> <div style="display: flex; align-items: center;"> <div style="margin-right: 20px;"> <p><b>Cathode</b></p> <p><b>Organic stack</b></p> <p><b>Anode</b></p> <p><b>Substrate</b></p> </div> <div style="text-align: center;"> </div> </div>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

COMPOUND-METAL CONTACTS FOR ORGANIC DEVICES AND  
METHOD FOR MAKING THE SAME

5 TECHNICAL FIELD

The present invention concerns a new class of contact materials used as electrodes for organic devices, such as organic light emitting diodes (OLEDs), organic displays and the like.

BACKGROUND OF THE INVENTION

10 Organic light emitting diodes (OLEDs) are an emerging technology with potential applications as discrete light emitting devices, or as the active element of light emitting arrays or displays, such as flat-panel displays. OLEDs are devices in which a stack of organic layers is sandwiched between two electrodes. At least one of these electrodes must be transparent in order for light - which is generated in the active region of the organic  
15 stack - to escape.

OLEDs emit light which is generated by organic electroluminescence (EL). Organic EL at low efficiency was observed many years ago in metal/organic/metal structures as, for example, reported in Pope et al., Journal Chem. Phys., Vol. 38, 1963, pp. 2024, and in "Recombination Radiation in Anthracene Crystals", Helfrich et al., Physical Review Letters,  
20 Vol. 14, No. 7, 1965, pp. 229-231. Recent developments have been spurred largely by two reports of high efficiency organic EL. These are C.W. Tang et al., "Organic electroluminescent diodes", Applied Physics Letters, Vol. 51, No. 12, 1987, pp. 913-915, and by a group from Cambridge University in Burroughs et al., Nature, Vol. 347, 1990, pp. 539. Tang et al. made two-layer organic light emitting devices using vacuum deposited  
25 molecular dye compounds, while Burroughs used spin coated poly(p-phenylenevinylene) (PPV), a polymer.

To date, virtually all OLED device structures have been built on glass substrates coated with indium-tin oxide (ITO), which serves as a transparent anode. The cathode is typically a low-workfunction elemental metal or alloy of such metals, e.g. Mg/Ag, Ca, or Al. Such cathodes are opaque. These low-workfunction elemental metals and alloys belong to the first class of cathode materials considered for OLEDs.

In order to enable a variety of possible applications, OLED structures suitable for opaque substrates (i.e. substrates other than the conventional glass substrates) are highly desirable. For example, if OLEDs could be fabricated on silicon, this would permit the use of an integrated active-matrix drive scheme. In such a structure light must be emitted through the uppermost layers of the device rather than through the substrate. One possible solution would be to build OLEDs by depositing the layers in the opposite order, which means a structure would be obtained with the transparent ITO anode deposited on top. This has proved difficult because of the harsh conditions under which the ITO is deposited, as reported by Zilan Shen et al. in "Three-Color, Tunable, Organic Light-Emitting Devices", Science, Vol. 276, 27 June 1997, pp. 2009-2011.

Alternatively, devices could be fabricated with the normal sequence of layers provided that a transparent cathode could be found. Gallium Nitride (GaN) has already been suggested as one possible cathode material, as disclosed and described in co-pending international patent application PCT/IB96/00780 with title "Gallium Nitride Based Cathodes for Organic Electroluminescent Devices and Displays". The international Filing date of this patent application is 8 August 1996. The GaN is a non-degenerate, wide-bandgap semiconductor (nd-WBS). As described in the co-pending application, all nd-WBSs have the advantage that their wide bandgap makes them transparent. It has been shown that the wide bandgap also leads to a favorable alignment of either the conduction band or valance band, or both, with the lowest unoccupied molecular orbitals (LUMO) or highest occupied molecular orbital (HOMO), respectively, of the organic material into which charge is to be injected. These non-degenerate, wide-bandgap semiconductors form a second class of cathode materials considered for OLEDs.

It has been shown that improved performance can be achieved when the energy levels of the electrode materials are chosen to match the energy levels of the respective molecular orbitals of the organic material into which it is supposed to inject carriers. By choosing optimized electrode materials the energy barriers to injection of carriers can be reduced.

- 5 With multilayer device architectures now well understood and commonly used, a major performance limitation of OLEDs is the lack of ideal contact electrodes. The main figure of merit for electrode materials is the position of their bands relative to those of the organic materials. In some applications it is also desirable for the electrode material to be transparent, as mentioned above. Furthermore, the electrode should be chemically inert and  
10 capable of forming a dense uniform film to ensure uniform injection and to effectively encapsulate the OLED.

There is a search for another class of materials which may serve as stable, possibly transparent cathodes and which are characterized by low-barrier or barrierless electron injection into OLEDs.

- 15 TiN, for example, is used in semiconductor technology on n-type silicon to form low barrier Schottky diodes, as described by M. Wittmer et al., in "Applications of TiN Thin Films in Silicon Device Technology", Thin Solid Films, Vol. 93, p. 397, 1982. TiN is also used in photo voltaic cells as an intermediate layer, as described in US patent 4,485,265, for example. TiN is employed in photo voltaic cells because it is less expensive and more  
20 abundant than other transition metals. The TiN is formed using chemical vapor deposition techniques at temperatures above 400°C.

It is an object of the present invention to provide new and improved organic light emitting devices, arrays and displays based thereon.

- It is an object of the present invention to find other materials which can be used as  
25 transparent electrodes of organic light emitting devices.

It is a further object of the present invention to provide organic light emitting devices with novel transparent electrodes.

It is another object of the present invention to provide a method for the formation of organic light emitting devices with novel transparent electrodes.

## SUMMARY OF THE INVENTION

The above objects have been accomplished by providing an OLED having a cathode comprising a metallic compound with low workfunction. Metallic compound or compound metal in the present context means any carbide, nitride, or boride of the early transition metals, lanthanides, and alkaline earths (group IIA), any mixture of these metallic compounds, or mixed carbides, nitrides and borides. The term early transition metal in the present context is meant to cover any elements of groups IIIB, IVB, VB, and VIB of the periodic table of elements. One example of such a metallic compound is titanium nitride (TiN). Metallic compounds are not meant to cover any alloys of elements that are already metals. These metallic compounds make up a whole new class of low-workfunction, semi-transparent, conducting materials very well suited as cathodes for organic devices.

The inventive approach capitalizes primarily on the inventor's finding that these metallic compounds are very well suited for efficiently injecting electrons into the organic layers of an OLED. The injection efficiency is correlated with the band lineup of metallic compounds and organics, a property which has been investigated and analyzed for the first time by the inventors. It has been found that the bands of the metallic compounds line up well at the compound-metal/organic interface. Experiments have revealed that the fermi energy of the metallic compounds is high enough to allow efficient injection of electrons.

Besides the finding that the fermi energy of metallic compounds is well aligned with the bands of organic compounds, there are other favorable characteristics of the metallic compounds, namely:

- relatively high conductivity,
- low absorbance and reflectance in the visible wavelength range of the electromagnetic spectrum (this makes the metallic compounds very different from the elemental metals also referred to as class 1 materials),
- reflectivity in the infrared, which protects the organics from heat during processing (heat mirror effect,

- high thermal stability,
  - due to low diffusivity of components and impurities, the metallic compounds also serve as a barrier to diffusion,
  - high corrosion resistance (chemical inertness), and
- 5    • extreme hardness.

It is important to note that the metallic compounds are metals and not nd-WBS semiconductors as the GaN proposed in the co-pending international patent application PCT/IB96/00780.

Advantages will become obvious from the detailed description and the drawings.

- 10    The metallic compounds can be used to make semi-transparent cathode OLEDs, a distinct advantage over the normally used opaque, low-workfunction elemental metals and alloys (class 1 metals) for fabricating OLED devices on silicon, where light must be extracted through the top of the device. In principle, semi-transparency can also be achieved with layers of class 1 metals if they would be made thin enough. The problem, however, would
- 15    be that these layers have to be made so thin that they do not have sufficient conductivity anymore. Such layers may not form a continuous film any longer and they may therefore lose their bulk properties. In general, there is a tradeoff between absorption of light and conductivity. Because the metallic compounds are both highly conducting and relatively weakly absorbing in the visible, this tradeoff is much more favorable.
- 20    In one embodiment of the present invention, a single or multilayer OLED structure having a metallic compound cathode directly in contact with the corresponding organic layer, and a conventional opposite contact electrode (anode) is envisioned.

- In another embodiment, an additional layer or stack of layers of transparent conducting metal oxide is deposited on top of the compound metal in order to provide for improved
- 25    lateral conductivity.

It is another advantage of the metallic compounds approach that due to its inherent simplicity it is less expensive than the class 1 metals or class 2 nd-WBSs. The stability to atmospheric exposure is also an advantage of the metallic compounds. Class 1 metals and alloys, in contrast, tend to be highly reactive with respect to water and oxygen.

- 5    Employing a transparent cathode in accordance with the present invention adds flexibility in the choice of anode designs, e.g. the anode can be opaque.

Some further advantages of the inventive approach are:

- a metallic compound cathode is chemically inert and thermally stable and therefore has no undesirable solid state interactions with the organic layers with which it is in contact  
10    or close proximity;
- a metallic compound is an outstanding encapsulant and mechanical protectant material for OLEDs;
- a metallic compound can be deposited at conditions required for OLED formation (e.g. low temperature, minimum damage to the growth surface) in a conductive state;
- 15    • a metallic compound has high infrared reflectivity, providing for protection of the organic compounds during deposition.

## DESCRIPTION OF THE DRAWINGS

The invention is described in detail below with reference to the following schematic drawings:

Fig. 1 is a schematic cross section of an organic light emitting diode, according to the present invention.

Fig. 2 is a schematic cross section of another organic light emitting diode, according to the present invention.

Fig. 3 is a schematic cross section of an organic light emitting array or display, according to the present invention.

## DESCRIPTION OF PREFERRED EMBODIMENT:

In the present context the expression metallic compounds or compound metals is meant to cover carbides, nitrides, and borides of the early transition metals, lanthanides, and alkaline earths (group IIA). The term early transition metal in the present context is meant to cover  
5 any elements of groups IIIB, IVB, VB, and VIB of the periodic table of elements.

Examples of such metallic compounds are:  $\text{CaB}_6$ ,  $\text{LaB}_6$ ,  $\text{TiC}$ ,  $\text{HfC}$ ,  $\text{TaC}$ ,  $\text{TiN}$ ,  $\text{ZrN}$ ,  $\text{HfN}$ , any mixture of these metallic compounds, or mixed carbides, nitrides and borides such as  $\text{TiC}_x\text{N}_y$ , for example.

The emphasis of the following description is on  $\text{TiN}$  which serves as an example out of the  
10 class of the metallic compounds.

A first embodiment of the present invention is described in connection with Figure 1. A schematic cross-section of an organic light emitting diode 10 is shown in this Figure. This diode 10 is formed on a substrate 11. This substrate 11 may be a silicon substrate for example. Any other substrate can be chosen. An anode 12 is formed on said substrate 11.  
15 ITO is well suited for this purpose. Directly on top of the anode 12 there is a so-called organic stack 13. This organic stack 13 at least comprises an organic layer in which electroluminescence takes place if an appropriate voltage is applied. Such an organic layer is usually referred to as an electroluminescent layer or emissive layer (EML). A  $\text{TiN}$  cathode 14 is situated on top of the organic stack 13. The thickness of the  $\text{TiN}$  cathode  
20 layer 14 is chosen to provide as high a transmittance as possible. Well suited is a thickness of 100 nm or less. In the present embodiment the  $\text{TiN}$  cathode is 50 nm thick. While bulk  $\text{TiN}$  is opaque and has a gold color, thin films of  $\text{TiN}$  can be prepared with transmittances well suited for OLED applications. A  $\text{TiN}$  layer of less than 50nm thickness has a transmittance above 50% in the wavelength range from 400 to 700nms. Exemplary details  
25 of the first embodiment are given in the following table (PPV means poly(p-phenylenevinylene)).

Layer	No.	Material	Thickness	present example
substrate	11	silicon	0.1mm-5mm	1mm
anode	12	ITO	10-2000nm	50 nm
organic stack	13	PPV	10-1000nm	200 nm
5 cathode	14	TiN	5-100 nm	50 nm

Note that the first embodiment is a cathode-up structure where light is emitted through the cathode 14 into the half-space above the device 10, as indicated in Figure 1.

If necessary for adequate lateral conductivity, an additional layer or stack of layers of transparent conducting metal oxide, such as ITO, could be deposited on top of the compound metal cathode. Such an ITO layer improves the lateral conductivity of the TiN cathode.

The stability, resistance to diffusion, and infrared reflectivity (heat mirror behavior) of the compound metal cathode protects the rest of the OLED structure 10 from the metal oxide deposition process if such an additional layer is deposited. The outstanding characteristics of the compound metal cathode furthermore provide for excellent protection of the OLED structure during the compound metal deposition.

Usually, the organic stack comprises several layers. Note that the layered structure of the organic stack is not shown in Figure 1.

Another embodiment of the present invention is illustrated in Figure 2. The shown device 20 is an anode-up device. From the substrate 21 up, listed in the order of deposition, is a glass/ITO/TiN/ETL/EML/HTL/Metal OLED structure. A low barrier to electron injection is obtained when employing a compound metal cathode 24.1 on an ITO layer 24.2. The conventional ITO anode can be replaced by a high work function metal since the anode 22 no longer serves as the transparent contact. Please note that light is emitted from the active region within the organic stack 23 through the metallic compound cathode 24.1 and ITO 24.2 and substrate 21. Please note that in the present embodiment the organic stack 23

comprises an electron transport layer (ETL), an electroluminescent layer (EML), and a hole transport layer (HTL).

In the following, exemplary details of the first embodiment are specified (Alq3 means tris(8-hydroxyquinolate)aluminum; TPD means N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine):

Layer	No.	Material	Width	present example
substrate	21	glass	0.1mm-5mm	1mm
10 cathode contact	24.2	ITO	5-100 nm	10 nm
cathode	24.1	TiN	10-100 nm	40 nm
ETL and EML		Alq3	10-1000nm	80 nm
HTL		TPD	5-500nm	50 nm
15 anode	22	Au	10-2000nm	100 nm

In the following, a display embodiment, based on and enabled by the present invention, is disclosed.

It would be advantageous if one could integrate OLEDs onto Si substrates because prior to OLED deposition, the substrate could be fabricated to contain active Si devices, such as for example an active matrix, drivers, memory and so forth. Such a structure, if realized in the Si, could be a very inexpensive, small-area, organic display with high resolution and performance.

An OLED, OLED array or an OLED display may either be grown directly on such a Si substrate carrying Si devices, or it may be fabricated separately and mounted onto the Si substrate later. A problem is the Si metallization. Cathode metals traditionally used in OLEDs (i.e. class 1 materials) are not stable under most Si processing conditions or in air. Another problem is that a transparent top contact is needed because Si is not a transparent substrate.

The present invention offers a solution to these problems. The disclosed metallic compound-based cathode permits a stable, low voltage contact to be formed on top of an organic stack situated on a silicon substrate. The inventive metallic compound-based cathodes are compatible with OLED on silicon technology.

- 5 An organic array or display structure formed on a Si substrate is illustrated in Figure 3 and described in the following. This display comprises a Si substrate 31 which has integrated circuits comprising active and/or passive devices such as memory cells, drivers, capacitors, transistor etc. (these devices are not shown in Figure 3).

10 On top of the Si integrated circuits, stable OLED anodes 32 (e.g. ITO, Au, Pt, Ni, Cr) are patterned. These anodes, together with the cathode layer 34 drive the organic stack 33 when a voltage is applied. The organic stack 33 is deposited in the cathode-up geometry on the patterned anodes 32 and Si substrate 31. Finally, a metallic compound cathode layer 34 is provided. It is to be noted that no details of the organic stack are shown for sake of simplicity. The cross-section of Figure 3 shows two adjacent OLEDs. These OLEDs may  
15 emit any color including blue or white.

More details of the array 30 are given in the following. The substrate 31 may be an Al-metallized Si chip on which the Al contacts are suitably modified to act as an anode. This Al-metallized Si chip serves as substrate for two OLEDs. These two OLEDs may be part of an OLED array or display. One such OLED comprises (from the bottom to the  
20 top):

- a stable anode layer 32,
- an organic stack 33 comprising an HTL, an organic doped or undoped active region (EML), and an ETL, and
- a TiN cathode 34

25 The cathode layer 34 is shown as a continuous layer in Figure 3. Likewise, this cathode layer 34 may be patterned.

The organic stack 33 of the present devices may - in addition to charge transport layers if needed at all - either comprise:

- a stack of more than one organic emission layer (EML), or
- an organic compound doped with one or more additives, organic or inorganic, chosen to dominate and enhance the electroluminescence, or
- a stack of more than one organic emission layer, some of which may be doped to dominate or enhance the electroluminescence of those particular organic emission layers, or
- a stack of more than one layer in which the role of one or more of said organic layers is to electrically confine one or more carrier types to improve the emission of an adjacent organic layer. Such a stack may also comprise inorganic, e.g. LiF, barrier layers.

TiN and the other compound metals can be deposited by a variety of techniques, including vacuum evaporation, E-beam evaporation, reactive sputtering, glow discharges, and chemical vapor deposition (CVD). It has been determined that the deposition on an OLED layer structure requires temperatures below 200°C. Even better suited are temperatures below 100°C. The higher temperature CVD processes are thus not well suited if TiN goes on top of the organic. Vacuum evaporation, E-beam evaporation, reactive sputtering, and glow discharges process, however, are well suited for the formation of compound metal cathodes on organic structures. TiN and the other compound metals have been proven to be compatible with organic manufacturing technology, if deposited at low enough temperatures. If an anode-up configuration is used, the compound metal is deposited prior to the organic layers, and harsher conditions may be used. TiN can be deposited by CVD at temperatures above 200°C, for example, directly onto the Si substrate to form cathodes on the metal contacts.

The preferred method for deposition of TiN cathodes is radio frequency (rf) reactive magnetron sputtering. Direct current (DC) reactive magnetron sputtering is also possible. In both cases, a mixture of Ar and N<sub>2</sub> is introduced into the sputter chamber, the ratio of

which is chosen to give the desired conductivity and transparency properties in the deposited film. Total chamber pressure, sputtering power, and target-to-substrate distance are additional, system-dependent parameters which must be optimized to give the desired film characteristics and minimize any damage to the substrate or organic films due, for example, to bombardment by ions or neutral species. If necessary, the substrate is cooled to avoid overheating during film deposition, but often this is not required.

In the following some examples of the different organic materials which can be used are given.

**Electron transport/Emitting materials:**

Alq<sub>3</sub>, Gaq<sub>3</sub>, Inq<sub>3</sub>, Scq<sub>3</sub>, (q refers to 8-hydroxyquinolate or its derivatives) and other 8-hydroxyquinoline metal complexes such as Znq<sub>2</sub>, Beq<sub>2</sub>, Mgq<sub>2</sub>, ZnMq<sub>2</sub>, BeMq<sub>2</sub>, BAlq, and AlPrq<sub>3</sub>, for example. These materials can be used as ETL or emission layer.

Other classes of electron transporting materials are electron-deficient nitrogen-containing systems, for example oxadiazoles like PBD (and many derivatives), and triazoles, for example TAZ (1,2,4-triazole).

These functional groups can also be incorporated in polymers, starburst and spiro compounds. Further classes are materials containing pyridine, pyrimidine, pyrazine and pyridazine functionalities.

Finally, materials containing quinoline, quinoxaline, cinnoline, phthalazine and quinazoline functionalities are well known for their electron transport capabilities.

Other materials are didecyl sexithiophene (DPS6T), bis-triisopropylsilyl sexithiophene (2D6T), Azomethin-zinc complexes, pyrazine (e.g. BNVP), styrylanthracene derivatives (e.g. BSA-1, BSA-2), non-planar distyrylarylene derivatives, for example DPVBi (see C. Hosokawa and T. Kusumoto, International Symposium on Inorganic and Organic Electroluminescence 1994, Hamamatsu, 42), cyano-substituted polymers such as cyano PPV (PPV means poly(p-phenylenevinylene)) and cyano PPV derivatives.

The following materials are particularly well suited as

**Emission layers and Dopants:**

Anthracene, pyridine derivatives (e.g. ATP), Azomethin-zinc complexes, pyrazine (e.g. BNVP), styrylanthracene derivatives (e.g. BSA-1, BSA-2), Coronene, Coumarin, DCM  
5 compounds (DCM1, DCM2), distyryl arylene derivatives (DSA), alkyl-substituted distyrylbenzene derivatives (DSB), benzimidazole derivatives (e.g. NBI), naphthostyrylamine derivatives (e.g. NSD), oxadiazole derivatives (e.g. OXD, OXD-1, OXD-7), N,N,N',N'-tetrakis(m-methylphenyl)-1,3-diaminobenzene (PDA), perylene and perylene derivatives, phenyl-substituted cyclopentadiene derivatives, 12-phthaloperinone  
10 sexithiophene (6T), polythiophenes, quinacridones (QA) (see T. Wakimoto et al., International Symposium on Inorganic and Organic Electroluminescence, 1994, Hamamatsu, 77), and substituted quinacridones (MQA), rubrene, DCJT (see for example: C. Tang, SID Conference San Diego; Proceedings, 1996, 181), conjugated and non-conjugated polymers, for example PPV and PPV derivatives (soluble precursor),  
15 dialkoxy and dialkyl PPV derivatives, for example MEH-PPV (poly(2-methoxy)-5-(2'ethylhexoxy)-1,4-phenylene-vinylene), poly(2,4-bis(cholestanoxyl)-1,4-phenylene-vinylene) (BCHA-PPV), and segmented PPVs (see for example: E. Staring in International Symposium on Inorganic and Organic Electroluminescence, 1994, Hamamatsu, 48, and T. Oshino et al. in Sumitomo Chemicals,  
20 1995 monthly report).

**Hole transport layers and Hole injection layers:**

The following materials are suited as hole injection layers and hole transport layers.

Materials containing aromatic amino groups, like tetraphenyldiaminodiphenyl (TPD-1, TPD-2, or TAD) and NPB (see C. Tang, SID Meeting San Diego, 1996, and C. Adachi et  
25 al. Applied Physics Letters, Vol. 66, p. 2679, 1995), TPA, NIPC, TPM, DEH (for the abbreviations see for example: P. Borsenberger and D.S. Weiss, Organic Photoreceptors for Imaging Systems, Marcel Dekker, 1993). These aromatic groups can also be incorporated in polymers, starburst (for example: TCTA, m-MTDATA, see Y. Kuwabara

et al., *Advanced Materials*, 6, p. 677, 1994, Y. Shirota et al., *Applied Physics Letters*, Vol. 65, p. 807, 1994) and spiro compounds.

Further examples are: Copper(II) phthalocyanine (CuPc),  
(N,N'-diphenyl-N,N'-bis-(4-phenylphenyl)-1,1'-biphenyl-4,4'-diamine), distyryl arylene  
5 derivatives (DSA), naphthalene, naphthostyrylamine derivatives (e.g. NSD), quinacridone  
(QA), poly(3-methylthiophene) (P3MT) and its derivatives, perylene and perylene  
derivatives, polythiophene (PT), 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA),  
PPV and some PPV derivatives,  
poly(2-methoxyl,5-(2'ethyl-hexoxy)-1,4-phenylene-vinylene (MEH-PPV),  
10 poly(9-vinylcarbazole) (PVK), discotic liquid crystal materials (HPT).

There are many other organic materials known as being good light emitters, and many more  
will be discovered. These materials can be used as well for making light emitting structures  
according to the present invention. More information on organic materials can be found in  
text books and other well known publications, such as the book "Inorganic and Organic  
15 Electroluminescence", edited by R.H. Mauch et al., Wissenschaft und Technik Verlag,  
Berlin, Germany, 1996, and the book "1996 SID International Symposium, Digest of  
Technical Papers", first edition, Vol. XXVII, May 1996, published by Society for  
Information Display, 1526 Brookhollow Dr., Suite 82, Santa Ana, CA, USA.

Additionally, blend (i.e. guest-host) systems containing active groups in a polymeric binder  
20 are also possible. The concepts employed in the design of organic materials for OLED  
applications are to a large extent derived from the extensive existing experience in organic  
photoreceptors. A brief overview of some organic materials used in the fabrication of  
organic photoreceptors is found in the above mentioned publication of P. Brosenberger and  
D.S. Weiss, and in Teltech, Technology Dossier Service, Organic Electroluminescence  
25 (1995), as well as in the primary literature.

Examples of inorganic barrier materials are LiF, CaO, MgO and so forth.

OLEDs have been demonstrated using polymeric, oligomeric and small organic molecules. The devices formed from each type of molecules are similar in function, although the deposition of the layers varies widely. The present invention is equally valid in all forms described above for organic light emitting devices based on polymers and oligomers, or  
5 small molecules.

Small molecule devices are routinely made by vacuum evaporation. This is compatible with the process used for the formation of the compound metal cathodes.

Evaporation can be performed in a Bell jar type chamber with independently controlled resistive and electron-beam heating of sources. It can also be performed in a Molecular  
10 Beam Deposition System incorporating multiple effusion cells and sputter sources. In these cases, the metallic compound deposition can occur in the same chamber, a vacuum connected chamber, or even a separate chamber if some atmospheric contamination is tolerable.

Oligomeric and polymeric organics can also be deposited by evaporation of their  
15 monomeric components with later polymerization via heating or plasma excitation at the substrate. It is therefore possible to copolymerize or create mixtures by co-evaporation.

In general, polymer containing devices (single layer, multilayer, polymer blend systems, etc.) are made by dissolving the polymer in a solvent and spreading it over the substrate either by spin coating or the doctor blade technique. After coating the substrate, the solvent  
20 is removed by evaporation or otherwise. This method allows the fabrication of well defined multilayer organic stacks, provided that the respective solvents for each subsequent layer do not dissolve previously deposited layers.

Additionally, hybrid devices containing both polymeric and evaporated small organic molecules are possible. In this case, the polymer film is generally deposited first, since  
25 evaporated small molecule layers cannot withstand much solvent processing.

More interesting is the possibility of making a polymer/inorganic transport layer on top of which monomeric layers are evaporated, possibly also incorporating mixtures. If the

polymer is handled in an inert atmosphere prior to introduction to vacuum, sufficient cleanliness for device fabrication is maintained. In any case, the chemical inertness of TiN and other metallic compound makes it highly tolerant of polymer OLED processing which is advantageous if the TiN is formed as bottom electrode before deposition or formation of the organic stack.

5

To summarize, the inventive metallic compound cathodes are fully compatible with polymeric, oligomeric, and small-molecule OLED designs, or any hybrid design thereof.

## CLAIMS

1. An organic electroluminescent device comprising a substrate, an anode, a cathode, and an organic stack being sandwiched between the anode and cathode, characterized in that the cathode comprises a metallic compound, wherein the metallic compound is a carbide, nitride, or boride of an early transition metal, lanthanide or alkaline earth.
2. The organic electroluminescent device of claim 1 in the case when the metallic compound is a carbide, nitride, or boride of an early transition metal, wherein the early transition metal is an element of group IIIB, IVB, VB, or VIB of the periodic table of elements.
3. The organic electroluminescent device of claim 1, wherein the cathode has a transmittance of at least 50% in the wavelength range between 400 nm and 700 nm.
4. The organic electroluminescent device of claim 1, wherein the cathode has a thickness less than or equal to 100 nm.
5. The organic electroluminescent device of claim 4, wherein the cathode has a thickness of about 50nm.
6. The organic electroluminescent device of claim 1, wherein the cathode comprises an additional layer which provides for improved lateral conductivity.
7. The organic electroluminescent device of claim 6, wherein the additional layer comprises indium-tin oxide (ITO).
8. The organic electroluminescent device of claim 1 having the following sequence of layers: substrate/anode/organic stack/cathode.
9. The organic electroluminescent device of claim 1 having the following sequence of layers: substrate/cathode/organic stack/anode.

10. The organic electroluminescent device of claim 8, wherein light is emitted through the cathode.
11. The organic electroluminescent device of claim 9, wherein light is emitted through the cathode and substrate.
- 5 12. The organic electroluminescent device of claim 1, wherein the organic stack comprises an emission layer (EML) and at least an electron transport layer (ETL) or a hole transport layer (HTL).
13. The organic electroluminescent device of claim 1, wherein said metallic compound is  $\text{CaB}_6$ ,  $\text{LaB}_6$ ,  $\text{TiC}$ ,  $\text{HfC}$ ,  $\text{TaC}$ ,  $\text{TiN}$ ,  $\text{ZrN}$ ,  $\text{HfN}$ , any mixture of these metallic  
10 compounds, or mixed carbides, nitrides and borides such as  $\text{TiC}_x\text{N}_y$ .
14. The organic electroluminescent device of claim 1 being an array or display.
15. The organic electroluminescent device of claim 14, wherein the substrate comprises active and/or passive devices.
- 15 16. Method for making an organic electroluminescent device comprising a substrate, an anode, a cathode, and an organic stack being sandwiched between the anode and cathode, and wherein the cathode comprises a metallic compound, which is a carbide, nitride, or boride of an early transition metal, lanthanide, or alkaline earth comprising the steps:
  - introducing into a sputter chamber a suitable ratio of any of the reactants  $\text{N}_2$ ,  
20  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{B}_2\text{H}_6$ ,  $\text{BF}_3$  selected to form the metallic compound and an inert gas,
  - performing a reactive sputtering process for the deposition of the metallic compound.
- 25 17. Method for making an organic electroluminescent device comprising a substrate, an anode, a cathode, and an organic stack being sandwiched between the anode and cathode,

and wherein the cathode comprises a metallic compound, which is a carbide, nitride, or boride of an early transition metal, lanthanide, or alkaline earth comprising the steps:

- introducing into a sputter chamber a sputter target comprising early transition metal, lanthanide, or alkaline earth selected to form the metallic compound,
- 5       • performing a non-reactive sputtering process for the deposition of the metallic compound using a carbide, boride, or nitride.

18. The method of claim 16 or 17, whereby the sputter process is a radio frequency (rf) magnetron sputter process.

10       19. The method of claim 16 or 17, whereby the sputter process is a direct current (DC) magnetron sputter process.

20. The method of claim 16, whereby the metallic compound to be formed is TiN, and whereby the inert gas is Ar and the reactant is N<sub>2</sub>.

1/3

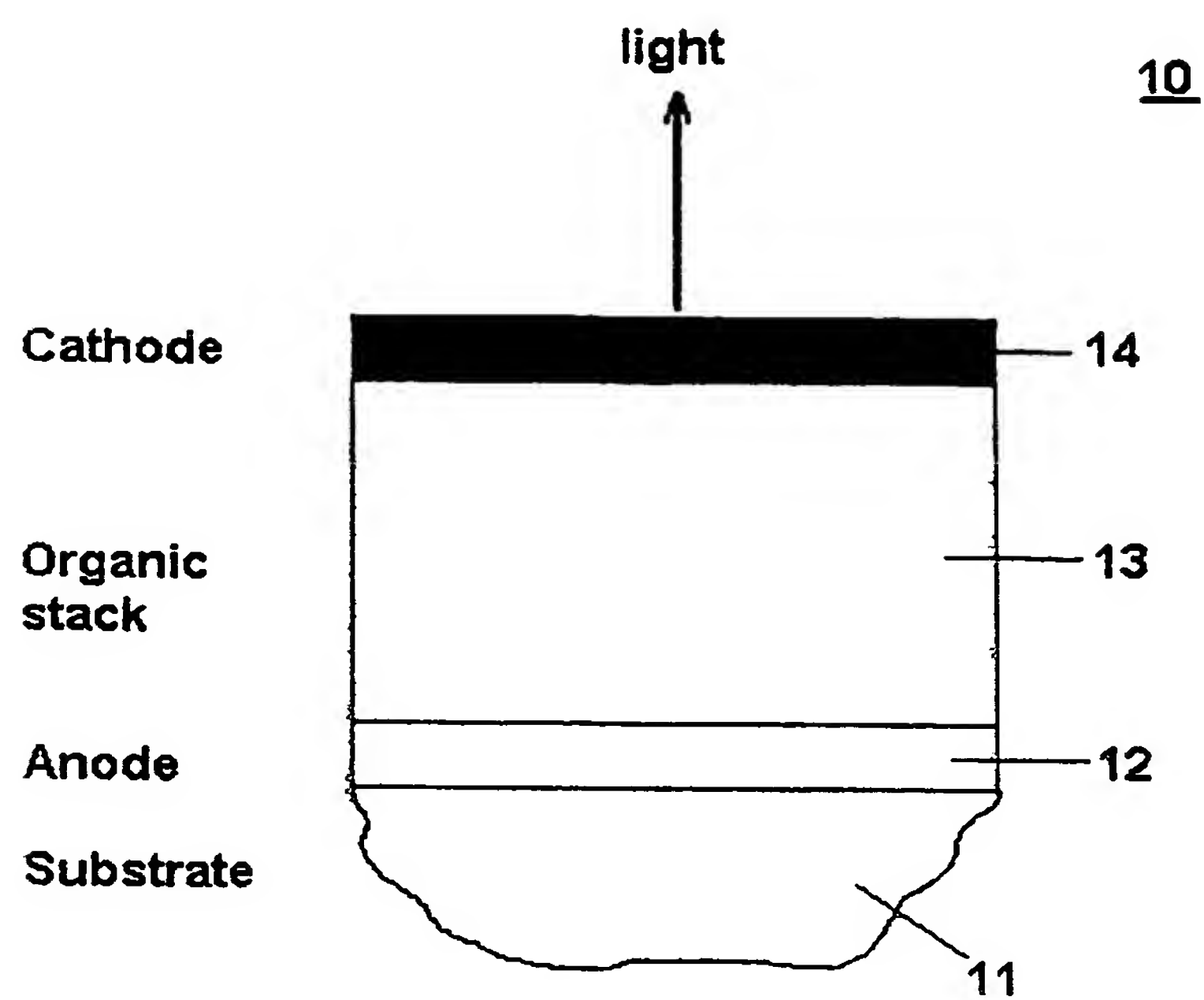
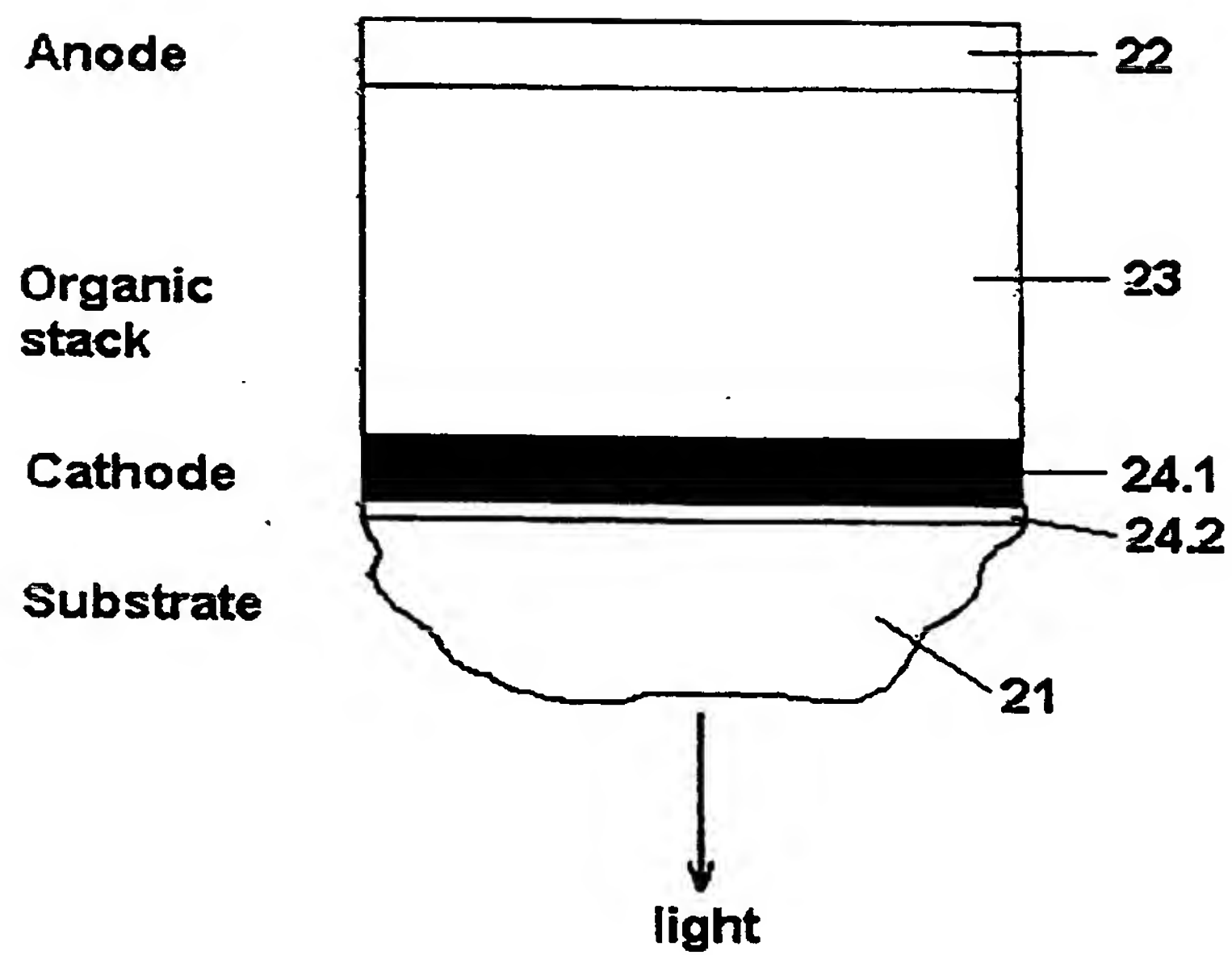


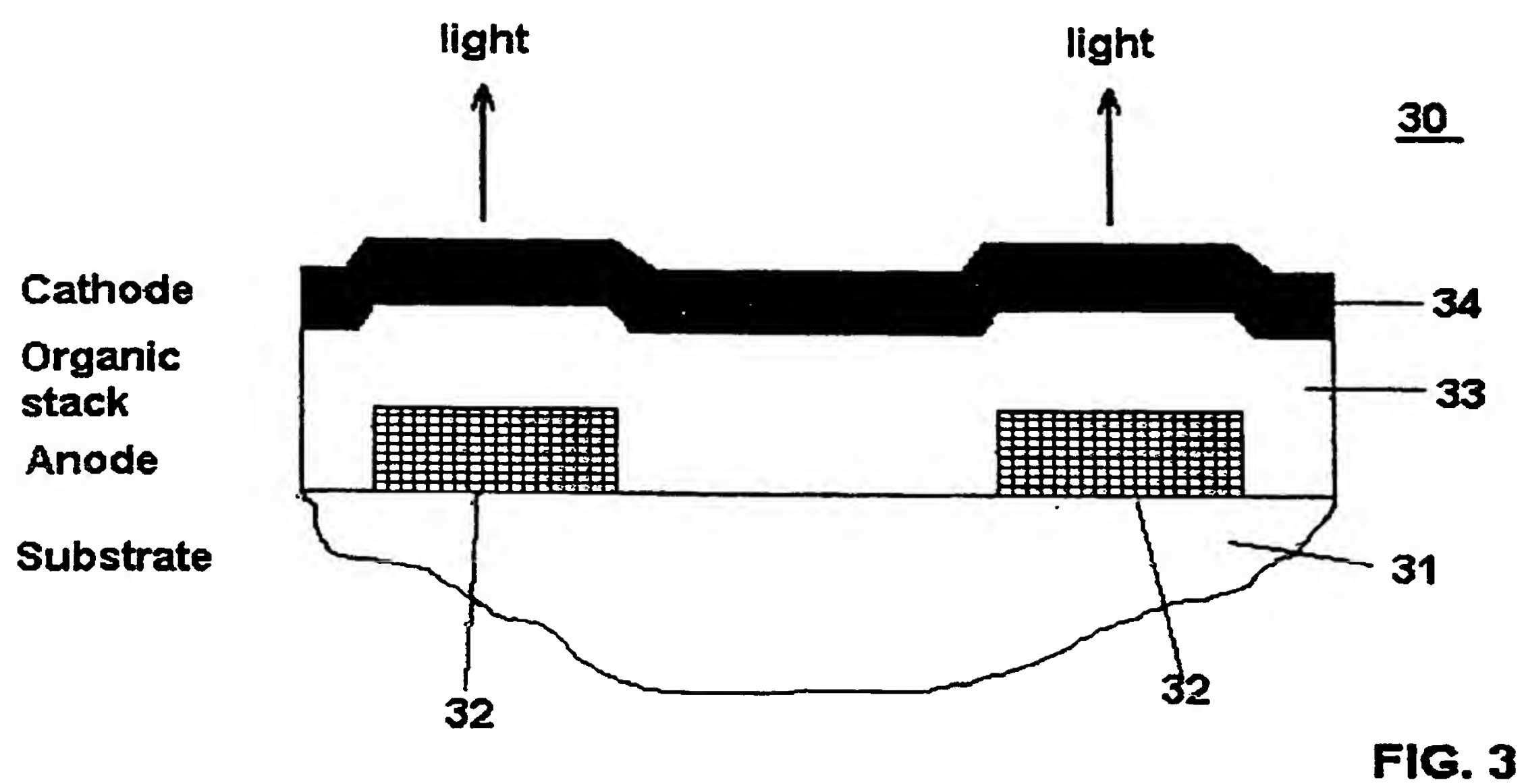
FIG. 1

2/3

20



**FIG. 2**



# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/IB 97/01565

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 H01L H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 729 191 A (EASTMAN KODAK CO) 28 August 1996  see the whole document	1,2,4,5, 8,9, 12-15
A	---	3,16-19
X	PATENT ABSTRACTS OF JAPAN vol. 095, no. 002, 31 March 1995 -& JP 06 310280 A (FUJI XEROX CO LTD), 4 November 1994 see abstract	1,2,9, 12,13
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 546 (E-1008), 4 December 1990 -& JP 02 234394 A (IDEMITSU KOSAN CO LTD), 17 September 1990 see abstract	1,2,8,13
	---	
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

3 August 1998

Date of mailing of the international search report

10/08/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

De Laere, A

INTERNATIONAL SEARCH REPORT

In .tional Application No  
PCT/IB 97/01565

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 47050 A (STRITE SAMUEL CLAGETT ;RIESS WALTER (CH); IBM (US)) 11 December 1997  -----	1,3-12, 14,15

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 97/01565

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0729191 A	28-08-1996	US 5608287 A JP 8288071 A	04-03-1997 01-11-1996
WO 9747050 A	11-12-1997	WO 9747051 A	11-12-1997